

CLAIMS

1. A process for the carbonylation of a conjugated diene by reacting the conjugated diene with carbon monoxide and a hydroxyl group-containing compound in the presence of a palladium catalyst system in a reaction zone to produce a reaction mixture, said catalyst system comprising (a) a source of palladium cations, (b) a mono-, bi- or multidentate phosphine ligand, containing at least one phosphorus atom which is directly bound to two or three aliphatic carbon atoms, as process ligand to produce a palladium-phosphine ligand complex catalyst, and (c) a source of anions, said process ligand (b) containing the moiety shown in formula (I):



wherein A¹ and A² each represent an aliphatic carbon atom which can be connected to one or more aliphatic or aromatic carbon atoms or both A¹ and A² are part of an at least 5-membered ring including the phosphorus atom, and X represents an aliphatic or aromatic carbon atom which can be connected to one or more aliphatic or aromatic carbon atoms or X is part of an organic bridging group connecting another identically or differently substituted phosphorus atom, and said source of anions (c) containing a carboxylic acid, characterized in that said process ligand is fed continuously or periodically into the process as ligand make-up at a temperature of 50°C or lower.

2. A process as claimed in claim 1, wherein the ligand make-up is added to a reaction mixture containing at least a portion of the catalyst system.

3. A process as claimed in claim 2, wherein said process is performed as a continuous process.

4. A process as claimed in any one of claims 1-3, wherein said process further comprises separating reaction product from said reaction mixture to obtain a catalyst mixture containing at least a portion of said catalyst system and recycling at least a portion of said catalyst mixture to the reaction zone.

5. A process as claimed in claim 3, wherein said process further comprises separating high boiling compounds and/or dead ligand from said catalyst mixture and recycling the mixture containing catalyst obtained in the high boiler purge/catalyst separation zone and/or obtained in the dead ligand/catalyst separation zone to the reaction zone.
6. A process as claimed in claim 4, wherein said ligand make-up is added to said catalyst mixture prior to feeding said catalyst mixture to the reaction zone.
7. A process as claimed in claim 5, wherein said ligand make-up is added to the mixture containing catalyst prior to feeding said mixture to the reaction zone.
- 10 8. A process according to claim 5, wherein said mixture containing catalyst is united with the catalyst mixture obtained in the process according to claim 3 prior to feeding said catalyst mixture to the reaction zone resulting in a united catalyst mixture and said ligand make-up is added to said united catalyst mixture.
9. A process according to any one of claims 1 to 8, wherein the concentration and degradation rate of the process ligand is monitored during the course of the carbonylation process and ligand make-up is added to the process in an amount that is equal to the amount of the consumed process ligand.
- 15 10. A process as claimed in any one of claims 1 to 9, characterized in that a second phosphine ligand different from said process ligand is fed continuously or periodically to the process, wherein said second ligand is chosen such that its phosphonium salt is reversible under carbonylation conditions.
11. A process as claimed in claim 10, characterized in that said second phosphine ligand contains at least one phosphorus atom which is connected to two aryl groups.
- 25 12. A process as claimed in claim 10 or 11, wherein said second phosphine ligand has less coordination strength to palladium than the process phosphine ligand.
13. A process as claimed in anyone of claims 10-12, wherein said second phosphine ligand is a triaryl phosphine or a bis(diarylphosphino)alkane.
14. A process as claimed in claim 13, wherein said second phosphine ligand is selected from the group consisting of triphenyl phosphine, a substituted triphenylphosphine, a trinaphthylphosphine, a substituted trinaphthylphosphine or
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a bis(diphenylphosphino)alkane derivative having 2-8 carbons between the phosphorus atoms, straight or branched.

15. A process as claimed in any one of claims 10-14, wherein said second phosphine ligand is fed to the process together with said ligand make-up.
- 5 16. A process as claimed in any one of claims 1-15, wherein the process ligand is selected from the group consisting of 2,3-bis(9-phosphabicyclononyl) butane, 1,2-bis(9-phosphabicyclononyl)ethane, 1,2-bis(9-phosphabicyclononyl)propane, 1,2-bis(carboxymethyl)-1,2-bis(9-phosphabicyclononyl)ethane, 1,2-bis(hydroxymethylene)-1,2-bis(9-phosphabicyclononyl)ethane, 1,2-bis(methoxymethylene)-1,2-bis(9-phosphabicyclononyl)ethane 1,2-bis(9-phosphabicyclononyl)cyclohexane, 1,2-bis(9-phosphabicyclononyl)benzene, 1,2-bis(9-phosphabicyclononyl)cyclopentane, 3,4-bis(9-phosphabicyclononyl)hexane, 2-bis(dicyclohexylphosphino)-3-(9-phosphabicyclononyl)butane, 1,2-dicyclohexyl-1,2-bis(9-phosphabicyclononyl)ethane and 1-cyclohexyl-1,2-bis(9-phosphabicyclononyl)ethane.
- 15 17. A process as claimed in any one of the preceding claims, wherein the process ligand is added in an organic solvent for said process ligand selected from the group consisting of an alkanol, a C₆-diester, or a mixture of two or more of these compounds.
- 20 18. A process as claimed in any one of the preceding claims, wherein the conjugated diene is 1,3-butadiene.
19. A process as claimed in any one of the preceding claims, wherein the hydroxy-group containing compound is methanol or ethanol.
20. A process as claimed in any one of the preceding claims, wherein the carboxylic acid is selected from the group consisting of pivalic acid, monomethyladipate, , 3-pentenoic acid, acetic acid or a mixture of two or more of these compounds.